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Thunderbolt in biogeochemistry: galvanic effects of lightning as another source for metal remobilization

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Iron and manganese are relevant constituents of the earth's crust and both show increasing mobility when reduced by free electrons. This reduction is known to be controlled by microbial dissimilation processes. Alternative sources of free electrons in nature are cloud-to-ground lightning events with thermal and galvanic effects. Where thermal effects of lightning events are well described, less is known about the impact of galvanic lightning effects on metal mobilization. Here we show that a significant mobilization of manganese occurs due to galvanic effects of both positive and negative lightning, where iron seems to be unaffected with manganese being abundant in oxic forms in soils/sediments. A mean of 0.025 mmol manganese (negative lightning) or 0.08 mmol manganese (positive lightning) mobilization may occur. We suggest that lightning possibly influences biogeochemical cycles of redox sensitive elements in continental parts of the tropics/subtropics on a regional/local scale.

Iron (Fe) and manganese (Mn) represent a major portion of the earth's crust[1,2] and are inherently involved in ecosystem processes[3]. The mobility of both elements is controlled mainly by redox conditions (e.g. iron wheel). Under oxic conditions Fe is abundant in an immobile trivalent form and Mn in an immobile tetravalent form where under anoxic conditions Fe and Mn are highly mobile. The reduction potential of these elements depends on the acquisition of electrons. During microbial organic matter decomposition in soils and sediments, organic matter is oxidized utilizing different electron acceptors e.g. oxygen, nitrate and sulfate[4,5] as well as Fe and Mn oxides[6,7] thus being reduced[3]. With the reduction of Fe^{3+} to Fe^{2+} and Mn^{4+} to Mn^{2+} the mobility of both metals increases where the metals will be mobilized and released from the sediment into the pore water. The same process occurs in the case of free electron supply. A natural source of free electrons is cloud to ground lightning including both thermal and galvanic effects[8,9] influencing e.g. nitrogen fixation as an important process in biogeochemistry[10]. It was found that thermal effects resulting from lightning are responsible for the reduction of redox sensitive elements such as phosphorus and iron in fulgurites[9,11]. However, less is known about the impact of the transferred energy charge by lightning (galvanic effect) on the mobilization of redox sensitive elements. During a lightning event an electron plasma channel is formed in which an electron flow from cloud to ground will occur[12]. The charge transferred from cloud to ground is different for positive lightning (16 coulomb (C)) in ~ 10% of all cases and negative lightning (5.2 C) in ~90% of all cases[13–16]. Furthermore, the lightning activity on earth is inhomogeneously distributed being highest in the tropics (up to 70 lightning flashes per km^2 and year[17]) whereas most of the ocean area remains unaffected. Hence, there are large differences in lightning activity on a regional scale. Because of the very high abundance of lightning events on earth[18] the mobilization of metals by galvanic lightning effects may be an important part of global and local biogeochemical cycling of redox sensitive metals.

Consequently, the influence of galvanic effects due to lightning activity on metal remobilization on a global and regional scale was estimated here for the first time by laboratory experiments and calculations on different scales.

Results

We found a significant impact ($p<0.001$) of lightning on Mn mobilization from soil/sediment to the water body/pore water comparing treatments with and without lightning (control treatment) (Fig. 1). However, no mobilization of Fe was found (always below limit of detection). The charge of lightning has a clear effect on metal mobilization. Increasing lightning charge strongly increases metal mobilization (Fig. S1). We also found an

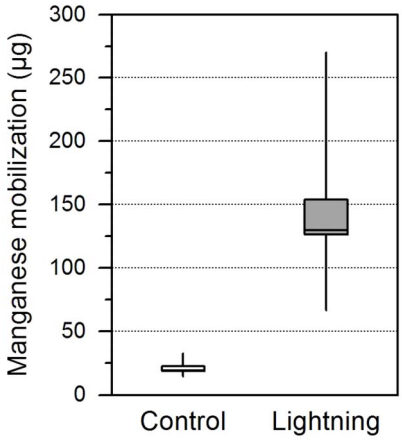

Figure 1 | Manganese mobilization from soil/sediment into soil water after lightning events in laboratory experiments at different charge per lightning compared to the control treatment without lightning ($p<0.001$).

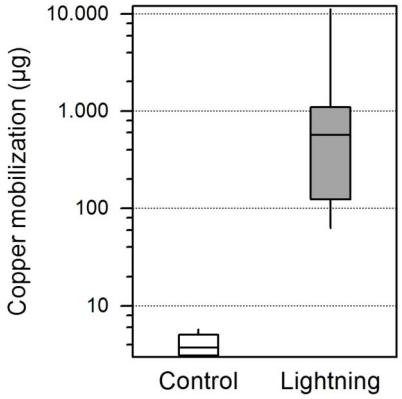

Figure 2 | Copper mobilization from soil/sediment into soil water after lightning events in laboratory experiments at different charge per lightning compared to the control treatment without lightning ($p<0.001$).

increasing copper mobilization with increasing lightning charge (Fig. 2). Furthermore, our measurements reveal that the polarity of lightning has no impact on mobilization/precipitation. Positive or negative lightning results in the mobilization of comparable amounts of elements. A calculated mean of 0.05 mmol of e.g. Fe (as an element requiring one electron for reduction) or 0.025 mmol of Mn (as an element requiring two electrons for reduction) may be electrochemically reduced and consequently mobilized by each lightning event with negative polarity (Table 1). In the case of a lightning event with positive polarity, a mean of 0.16 mmol of Fe and 0.08 mmol of Mn may be electrochemically reduced and consequently mobilized (Table 1) (see also Fig. 3).

Taking into account the inhomogeneous distribution of lightning activity on earth, a maximum mobilization of 0.12 g Mn km^{-2} a^{-1} (0.09 g Mn km^{-2} a^{-1} mobilization from negative lightning plus 0.03 g Mn km^{-2} a^{-1} from positive lightning) and of 0.24 g Fe km^{-2} a^{-1} (0.18 g Fe km^{-2} a^{-1} mobilization from negative plus 0.06 g Fe km^{-2} a^{-1} from positive lightning) is calculated based on a maximum of 70 lightning events per km^2.

Discussion

An important and intriguing outcome of our experiment is the significant manganese mobilization by galvanic effects of lightning (Fig. 1). Based on the one billion cloud-to-ground lightning events per year occurring on earth[19] and considering the natural distribution of negative/positive lightning (~ 9 : 1)[13,16] a maximum global mobilization of 1692 kg Mn or 3439 kg Fe per year may occur (Table 1) depending on element distribution and redox status. Nevertheless, this amount of global Mn and/or Fe mobilization by lightning activity is very small compared to the amount cycled by global biogeochemical processes[3,18]. The reduction of manganese oxides and iron oxides to divalent forms and not further to metal ions can be explained as follows: We used a nature-like soil-water system with a slightly acidic pH (comparable to rain water). Thus, in the system hydrogen ions are present. In aqueous systems the reduction of Fe^{2+}/Mn^{2+} becoming elementary is in both cases impossible because of the negative redox potential compared with standard hydrogen potential. In contrast, the reduction of manganese oxides and iron oxides to Fe^{2+} or Mn^{2+} in the aqueous system is thermodynamically possible. The fact that we observed manganese in the aqueous solution but not iron could be explained by the preferred reduction of manganese oxides due to the higher redox potential of this reaction. Our calculations of galvanic effects of lightning on element mobilization require no complex parameter calculations as for thermal effects[9], but are based on the transferred charge by lightning events. Beside thermal effects as source for elemental reduction[9] the galvanic effects revealed in our experiment show a clear impact on the mobilization of elements via reduction. The thermal effects forming fulgurites have a low impact on the mobilization of elements via reduction. This may be in contrast to galvanic effects, which are not limited to the fulgurites but also possibly affect the surrounding areas. However, more redox sensitive elements will always be remobilized first as suggested by the strong mobilization of manganese while iron seems to be unaffected by galvanic lightning effects. The very high recovery rate (up to 99%) of metal mobilization by lightning compared to the calculated mobilization in relation to lightning charge supports the assumption of element mobilization by lightning based on Faraday's laws (data not shown). An experimental side-effect is the high mobilization of copper from the anode and the ignition wire (anode effect) strongly increasing with lightning charge (Fig. 2). This can be explained by the higher extension of the plasma channel (higher electron flow) due to higher charges causing a strong electron transport through a small cross section directly to the copper anode and subsequently electrolysis[20,21].

For the hotspots of lightning activity in the continental parts of the tropics/subtropics on a local or regional scale a considerable impact

Table 1 | Mobilization potential for iron and manganese by lightning activity on earth, based on calculations using the above described formula

negative lightning (at 90% of cases)			positive lightning (at 10% of cases)		
at 5.2 C	0.00005	mol per lightning	at 16 C	0.00016	mol per lightning
	45.89	kmol a^{-1} on earth		15.69	kmol a^{-1} on earth
at 5.2 C	0.0028	g Fe per lightning	at 16 C	0.0089	g Fe per lightning
	2563	kg Fe per year		876	kg Fe per year
at 5.2 C	0.0014	g Mn per lightning	at 16 C	0.0044	g Mn per lightning
	1261	kg Mn per year		431	kg Mn per year

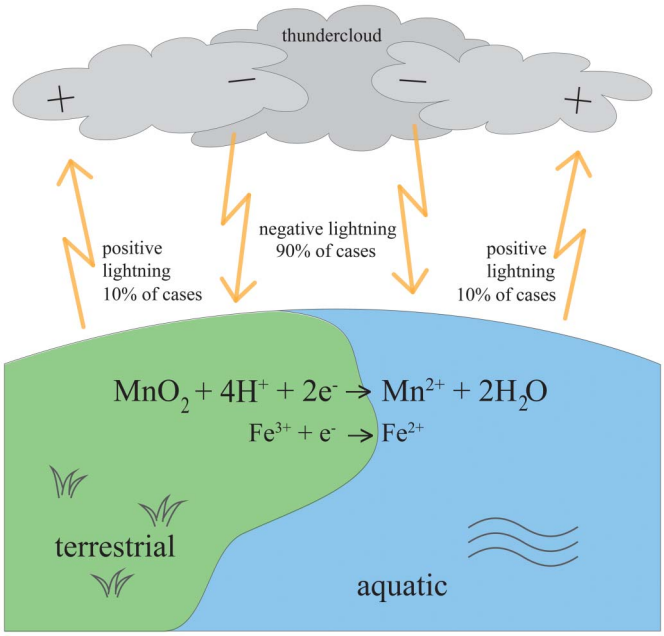

Figure 3 | Scheme of the biogeochemical processes affected by lightning activity.

on Fe/Mn mobilization/cycling can be estimated. Still the mobilization of elements even local scale (per km^{-2}) is small[3].

Such a mobilization of Fe/Mn (and possibly phosphorus bound to iron(III)) by galvanic lightning effects may affect the biogeochemistry of ecosystems with nutrient deficiency (e.g. Fe, Mn, P)[3,22] as shown previously[22]. This impact of lightning on biomass production due to effects on biogeochemistry is especially true for ecosystems of the tropics/subtropics[23–25].

Our measurements and estimates reveal a noticeable impact of lightning activity by galvanic effects on the mobilization of redox sensitive elements such as Fe/Mn on a local scale. Consequently, this process has to be considered in biogeochemical studies and modeling. The described galvanic process may also occur for all other redox sensitive elements (C, N, P, S, Cr, Co, As, Sb, Se, Hg, Tc and U)[26] and may alter their biogeochemical cycling characteristics.

Methods

To analyze the impact of galvanic lightning effects on Mn and Fe remobilization in soils or sediments, experiments were conducted under nature like conditions (sandy soil supernatant rain water to simulate conditions after intense rain). An analytical vessel was connected to a high current pulse generator. The vessel consists of an aluminum (Al) forged tube of 1.5 cm wall thickness, 35 cm inner diameter and 70 cm height. The bottom and top of the vessel were closed with a 2 cm thick Al-plate. The whole vessel inside was isolated by polyethylene film. A copper cathode (top) and copper anode (bottom) inside the analytical vessel had a distance of 35 cm and were connected by a thin copper ignition wire. Hence, only less than the half of the volume in the analytical vessel was filled with water and sand and the rest of the vessel served as compensatory volume to absorb the pressure resulting by lightning. This ignition wire enables initial electron flow from cathode to anode. The dimensions of the analytical vessel were chosen to optimize the water and soil volume in relationship to the occurring pressure. In order to conduct the experiments under nature like condition and also prevent destructive electro-hydraulic effects by lightning arcs it was chosen to limit the charging voltage of the condensators to values of about 6 kV. Five liters of sand and three liters of water were uniformly distributed on the anode around the ignition wire but with 5 cm distance to the cathode. The sandy soil originated from a sandpit (Dresden, Germany) was soaked with artificial rain water with pH = 5.6 and low soluble minerals concentration (Table S1). Prior to the experiment the sand was carefully washed, dried and stored until start of experiments. The sand had a quite low metal content (Table S1). After filling the analytical vessel with soil and water, it was closed and the lightning strikes were conducted at 4 to 6 kV and charges of 0.007 to 32 C within a few microseconds. The lightning currents were delivered by a CLR – current pulse generator. The condensators of the generator are connected in parallel, low- inductive configuration. By charging voltages up to 10 kV it is possible to deliver 10/350 µs shaped lightning currents with amplitudes up to 200 kA with this setup[27]. For conducting positive lightning a reverse electric polarity was used. Water samples were taken randomly five minutes after closing the analytical vessel and conducting the lighting and filtered by cellulose acetate filters (pore diameter 0.45 µm). Then water samples were divided afterwards. One aliquot was immediately analyzed for ferrous iron. The other part was acidified with HNO_3 (analytical grade, Carl Roth Germany). For the sand substrate characterization prior to the experiment, it was subjected to an *aqua regia* extraction according to Ref.28, using a CEM Mars5 microwave digestion system (CEM Corporation, Matthews, NC, USA). The elemental contents of waters and solid sample digests were determined by ICP-MS (PQ exCell instrument, Thermo Fisher Scientific Inc.) according to Ref.29. In addition, the water ferrous iron concentration was analyzed immediately after the experiment according to Ref.30. All chemicals were of analytical grade. Student's *t*-test was applied to compare the data using SPSS 16.01.

The calculations on the chemical elements mobilized by a change in electric charge (galvanic lightning effects) are based on Faraday's laws:

$$\delta_{mol}\mathrm{Me} = \frac{\text{Charge of lightning (C)}}{\text{Z * Faraday constant}}$$

δ_{mol}Me is the amount of remobilization of a metal and Z the charge number change. According to the known soil chemical redox pairs Z is one for the transfer from ferric to ferrous iron, and two for the release of divalent Mn from Mn-dioxide. C refers to the released charge per lightning event (16 C for positive and 5.2 for negative lightning) and the Faraday constant (F) of 96485.3365 C mol^{-1}. For the estimation of the global annual mobilization of Mn and Fe by reduction due to a shift in energy charge, 30 cloud-ground lightning events per second are chosen[19]. The calculation was done on a hypothetical assuming that all transferred charge is used to reduce Fe^{3+} to Fe^{2+} or Mn^{4+} to Mn^{2+}, because this is the maximum effect depending on redox status or element domination in the affected soils/sediments, for the most abundant redox sensitive metals in natural soils/sediments.

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Author contributions

J.S. and A.W. designed the experiment, conducted the experiment and wrote the manuscript. F.B. supplied the lightning laboratory equipment and gave comments to the manuscript. All authors reviewed the manuscript.

Additional information

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